

A REEXAMINATION OF THE GREENHOUSE EFFECT DUE TO CFC-11 AND CFC-12

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Abstract—Employing the most recent laboratory absorption-coefficient data¹ on the thermal infrared (i.r.) bands of CFC-11 (CFCl_3) and CFC-12 (CF_2Cl_2), which were measured at several temperatures relevant to the troposphere and the stratosphere, the greenhouse effect produced by these two CFCs has been reexamined. The effect upon the atmospheric radiative fluxes due to the temperature dependence of the absorption coefficient, especially in the many hot bands present in this spectral region, has been studied. The validity of the often used optically-thin approximation has been scrutinized in view of the observed enhancement in the absorption by the CFCs at low temperatures. The influence of absorption by water vapor on the radiative transfer through columns of CFC-11 and CFC-12 has also been considered. It has been shown that, even though each of these individual refinements may modify the previously estimated effect due to the CFCs by a small amount only, the collective effect may be a non-negligible 35% change in the surface-troposphere heating for every ppbv of CFC-11 and CFC-12 each introduced into a model atmosphere.

INTRODUCTION

Ramanathan² was the first to suggest that the strong absorption bands of CFC-11 (CFCl_3) and CFC-12 (CF_2Cl_2) in the atmospheric window region (8–12 μm) will contribute to the enhanced greenhouse effect produced by an increase in the atmospheric concentrations of anthropogenic trace gases. Since then, numerous other investigations have followed.^{3–13} The authors of none of these studies, however, have paid proper attention to the temperature dependence of the CFC-11 and CFC-12 absorption bands, especially of the many accompanying hot bands, perhaps due to the lack of experimental spectroscopic data at the relevant atmospheric temperatures.

It has long been recognized that the atmospheric transmittance through columns of trace gases cannot be determined from laboratory measurements at room temperature alone.¹⁴ At lower temperatures, the contributions from hot bands, which represent absorption of photons that results in transitions from an excited state with nearly the same energy as is involved in the ground state bands, are smaller. If hot bands were not present, the band strength S_ν ($\text{cm}^{-2} \text{atm}^{-1}$) per atmosphere of the absorbing gas would be inversely proportional to the temperature T , thus making $S_\nu T$ a constant.

The variation of the band strength with temperature affects the optically-thin model more directly than any other model used for describing the absorption by these bands. With the exception of Ramanathan et al.,⁶ it would seem that it had been the practice among the many modelers to assume that the absorption due to CFC-11 and CFC-12 falls within the so-called optically-thin limit. It is evident from Figs. 3, 6–18 of Ref. 1 that the absorption coefficients can be significantly larger at low temperatures than at room temperatures. Thus, the accuracy of the optically-thin approximation for the projected future, if not for the currently established volumetric mixing ratios of CFC-11 and CFC-12 in the atmosphere, cannot be determined *a priori*.

The purpose of the present paper is two-fold. First, we wish to determine if the modeling of the radiative forcing due to the 9.2 and 11.8 μm bands of CFC-11 and the 8.6, 9.1 and 10.8 μm bands of CFC-12 is refined by the explicit introduction of the temperature dependence of the absorption

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coefficient. Secondly, we examine whether or not relaxation of the optically-thin approximation, in lieu of the observed magnification of the absorption coefficients at low temperatures, has any effect on the computed radiative fluxes. Since the absorption-coefficient data on these bands at several temperatures of the troposphere and the lower stratosphere have become available only recently,^{1,14,15} such a reexamination seems appropriate at this time.

SPECTROSCOPIC DATA

A comprehensive review of the laboratory measurements published so far on the thermal i.r. spectra of CFC-11 and CFC-12 may be found in Varanasi¹ and Varanasi and Chudamani.¹⁴ The rotational structure in the CFC bands is so dense that any difference in the spectral transmittance would hardly be discernible at atmospheric pressures anywhere except in the central Q -branches when observed with spectral resolutions that varied between 0.4 and 1.0 cm^{-1} . This circumstance was clearly demonstrated in Figs. 2–4 of Ref. 1. Even though the central Q -branch profiles may still be subject to instrumental distortion if the spectral resolution were lower than 0.01 cm^{-1} , away from the central peaks, as is shown in Fig. 4 of Ref. 1, the absorption coefficient remains essentially invariant for a wavenumber interval of almost 0.1 cm^{-1} , thereby suggesting that the data obtained using grating and Fourier-transform spectrometers of moderate resolution (0.1 cm^{-1}) are fairly accurate. Lowering the spectral resolution introduces discernible distortion only near the central peaks of the absorption bands, as can be seen from the data shown in Figs. 11–13 of Ref. 1 that were obtained with spectral resolutions varying between 0.4 and 1.0 cm^{-1} . The distortion is minimal, however, in the sense that it is limited to a very narrow range of wavenumbers near the center, an effect that goes all but unnoticed in applications of the data to climate models.

The spectral absorption-coefficient data employed in the present investigation appear in Figs. 6–13 of Ref. 1, where they are compared in Figs. 14–18 with the measurements by other authors.^{15,16} Our choice of the laboratory data is based upon a critical examination¹ of all of the published low-temperature measurements.^{1,15–18} The laboratory spectra reported by McDaniel et al.¹⁵ were recorded with a spectral resolution of 0.03 cm^{-1} using a Fourier transform spectrometer and are now a part of the 1992 HITRAN Tape.¹⁷ The data, presented as cross sections in units of $\text{cm}^2\text{-molecule}^{-1}$, were obtained at 203, 213, 233, 253, 273, and 293 K. At each temperature, even though the spectra were collected at several pressures between 0.25 and 2.0 torr, the final data appearing in Refs. 15 and 17 are cross-sections corresponding to zero absorber amount. It is important to note that the rotational structure apparent in the data of McDaniel et al.^{15,17} (Figs. 14–17 of Ref. 1) is due to the extremely low pressures used. The facts that these data do not show the broadening effect demonstrated in Figs. 2–4 of Ref. 1 and that they were obtained with pure CFC samples at pressures too low compared to those of the troposphere and the lower stratosphere must be kept in mind in evaluating the comparison shown in Figs. 14–17 of Ref. 1. The data of Ref. 15 are in excellent agreement with the data of Ref. 1 in spectral regions where the rotational structure is not significant. In regions where line structure is evident, the data are consistent within the realm of pressure-broadening. This comparison suggests that the effect of pressure-broadening must be weighed carefully while using the data on the HITRAN Tape.¹⁷ The authors of Ref. 16 have reported absorption-coefficient data for CFC-12 only from 800 to 1200 cm^{-1} at 296 and 200 K. The absorption profile at 200 K presented in Ref. 16 is narrower than that measured in Ref. 1 at 205 K. The disagreement is attributed to some systematic errors.¹ The measurements of Nanes et al.,¹⁸ being limited to 216 and 294 K, are hardly adequate for the present study.

RADIATION MODELS

In atmospheric radiant flux calculations, an important parameter is the band absorptance which is defined as¹⁹

$$A(u) = \int_{-\infty}^{\infty} (1 - e^{-k_v u}) dv, \quad (1)$$

where the integration limits on the wavenumber v refer to the spectral region occupied by the vibration-rotation band under consideration and over which the measured absorption coefficient

k_v has sensible values. Here, u is the absorber amount appropriate for the atmospheric column of the trace gas and has the units of cm-amagat, which is abbreviated to cm-am.

In the optically-thin limit,

$$A(u) \approx S_v u, \quad (2)$$

since the band strength S_v is the integral of the spectral absorption coefficient over the spectral region occupied by the band.

As stated earlier, for conditions which are typical of the troposphere and the lower stratosphere, the absorption bands of CFC-11 and CFC-12 consist of spectral lines which are significantly wider than their spacing.¹ Thus, the rotational fine structure of the band is smeared out and the spectral absorption coefficient becomes a slowly varying function of the wavenumber,¹⁹ so much so that it is virtually a constant over a narrow wavenumber interval $\Delta\nu$, which we choose to be 0.5 cm^{-1} in the present calculations in order to be consistent with the spectral resolution which varies between 0.4 and 1.0 cm^{-1} in Ref. 1. The mean value \bar{k}_v over each wavenumber interval $\Delta\nu$ would then be consistent with the spectral absorptance coefficients measured in the laboratory.

Following Rodgers and Walshaw,²⁰ the temperature dependence of the absorption coefficient for each interval may be represented by

$$\bar{k}_v(T) = \bar{k}_v(T_0) + a_v(T - T_0) + b_v(T - T_0)^2, \quad (3)$$

where T (K) is the temperature, T_0 the reference temperature, and a_v and b_v the temperature correction coefficients, which are determined by least-squares fitting of the laboratory measurements of Ref. 1.

The measured absorption coefficient may also be viewed as a narrow-band model parameter as, for example, in the random-band models of Goody²¹ and Malkmus.²² In the smeared-out line structure limit,¹⁹ the absorption coefficient given by both the Goody and Malkmus models reduces to

$$\bar{k}_{\Delta\nu} = S_{\Delta\nu} / \Delta\nu. \quad (4)$$

$S_{\Delta\nu}$ is the sum of the line intensities within the interval $\Delta\nu$. $\bar{k}_{\Delta\nu}$ is the same as the average absorption coefficient \bar{k}_v . While for homogeneous paths and in the absence of overlapping by the bands of other absorbers k_v and $\bar{k}_{\Delta\nu}$ are equivalent, for inhomogeneous paths, an appropriate scaling approximation²⁰ may be required to use Eq. (4).

When the only available spectroscopic data are the total band intensities, the modeler may often resort, especially in cases where the absorber amounts are quite small, to the optically-thin approximation of Eq. (2). If the absorber amounts exceed the linear limit of Eq. (2), a proper curve-of-growth [$A(u)$ vs u] is usually determined either experimentally or in terms of a band model. In the present study, by using the experimental absorption coefficients k_v of Ref. 1 and Eq. (1), we have computed the band absorptances $A(u)$ needed for atmospheric calculations and refer to them hereafter as *exact* values of the band absorptance.

We compare in Figs. 1 and 2 these exact values of A at 300 K with those obtained using Eq. (6) and the results of Ramanathan et al.⁶ obtained by employing a band model. In Fig. 1 we present the deviations between the two models [Eq. (6) and Ref. 6] and the exact values for the case of CFC-11. Figure 2 contains similar deviations for CFC-12. The optically-thin approximation yields results within 3% for CFC-11 amounts less than 10^{-3} cm-am and within 1.5% for CFC-12 amounts less than 10^{-3} cm-am. Thus, the optically-thin approximation appears to hold as long as the CFC-11 and CFC-12 mixing ratios are below 1.25 ppbv, which correspond to column amounts of 10^{-3} cm-am. The current mixing ratios are well below this limit in the atmosphere. The 1985 values were 0.22 and 0.375 ppbv, respectively, for CFC-11 and CFC-12.^{12,23,24} If the Montreal Protocol¹³ on the phasing-out of the use of CFC-11 and CFC-12 in industrial and other applications were universally honored and future concentrations of these two CFCs could be maintained at about their current levels, relaxation of the optically-thin approximation would clearly be unnecessary.

For absorber amounts $u \gg 10^{-3}$ cm-am, the deviation between the optically-thin approximation and the exact band absorptance is nearly exponentially dependent on u (Figs. 1–2). It has already been cautioned in Ref. 6 that for a CFC-11 mixing ratio of 2 ppbv, the optically-thin limit would begin to break down. Since the results of Ref. 6 are based on a band model and involve

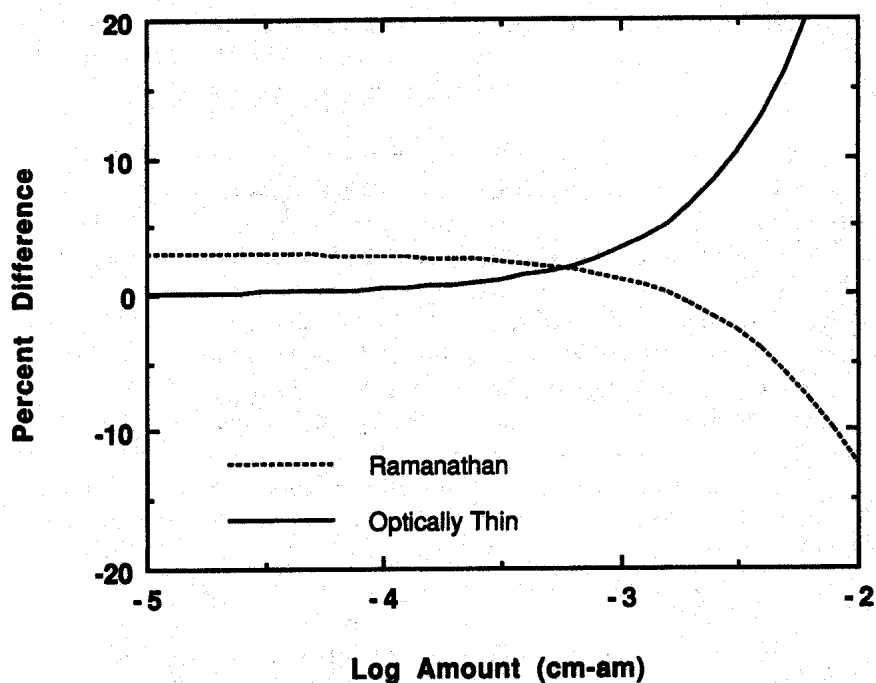


Fig. 1. Comparison of the values of the total band absorbance due to the 9.2 and 11.8 μm bands of CFC-11 calculated for the optically-thin approximation and the model of Ramanathan et al.⁶ with the *exact* values calculated by using the experimental spectral absorption coefficients of Ref. 1.

extrapolation into a region of a curve-of-growth that was not based on laboratory data obtained at conditions appropriate to the atmosphere, we view the evidence presented in Figs. 1 and 2, which is based upon accurate laboratory data on the absorption coefficients, to be more definitive and providing experimental support to what was purely a theoretical suggestion by Ramanathan et al.⁶ It was noted in Ref. 12 that the atmospheric abundance of chlorine (about 3 ppbv) will at least

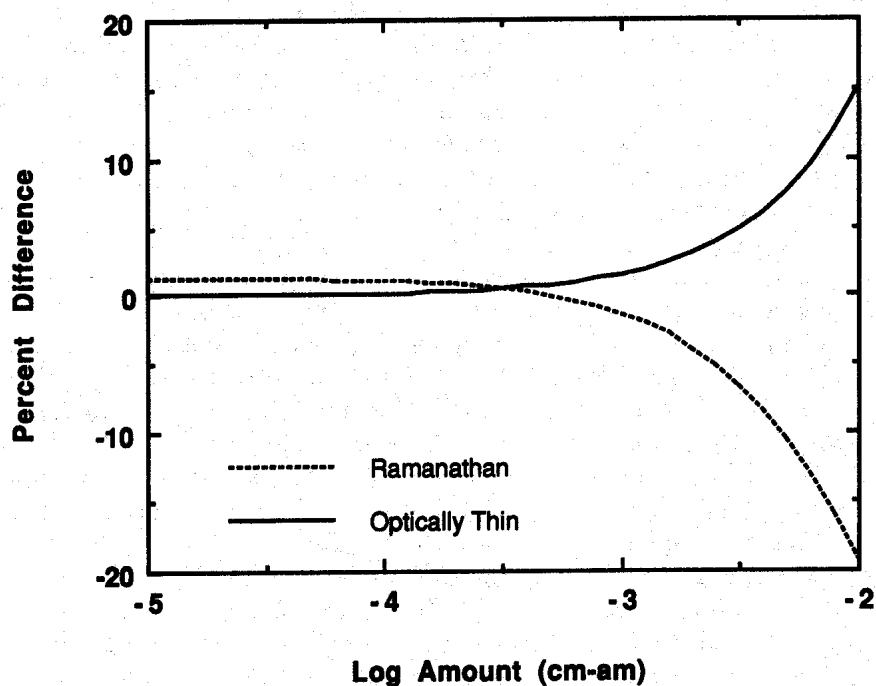


Fig. 2. Comparison of the values of the total band absorbance due to the 8.6, 9.1, and 10.8 μm bands of CFC-12 calculated for the optically-thin approximation and the model of Ramanathan et al.⁶ with the *exact* values calculated by using the experimental spectral absorption coefficients of Ref. 1.

double to triple during the next century under the best of conditions. If an implication of this statement were to be that projected concentrations of these two and other CFCs could be tripled, the present scrutiny of the optically-thin approximation may prove to be of value in the assessment of future scenarios of global warming.

We also present in Figs. 1 and 2 the difference between the band absorptances derived by Ramanathan et al.,⁶ who employed essentially the exponential-sum fitting method of Wiscombe and Evans,²⁵ and the exact $A(u)$. For $u \leq 10^{-4}$ cm-am, the band absorptances derived by Ramanathan et al.⁶ are larger by ~ 3 and 1.2%, respectively, for CFC-11 and CFC-12 than the values we have obtained. This discrepancy is the direct consequence of the fact that the band intensities used by Ramanathan et al. are larger than those used by us by the same percentages. If the same band strengths were used in the two computations, the discrepancy would disappear. On the other hand, for $u \geq 10^{-3}$ cm-am, the model used by Ramanathan et al.⁶ yields values of $A(u)$ which are not only progressively smaller than the exact values but also exhibit a different slope with respect to u . Since an absorber amount of 8×10^{-4} cm-am corresponds approximately to a mixing ratio of 1 ppbv, it would seem that at these and larger absorber amounts the model of Ramanathan et al.⁶ provides an erroneous representation of the sign as well as of the magnitude of the deviation of $A(u)$ from the optically-thin approximation. This fact will have a direct bearing on the computed radiative forcing of the CFCs.

ATMOSPHERIC-FLUX CALCULATIONS

The importance of the radiative forcing of CFC-11 and CFC-12 lies in the modification produced by their absorption bands on the net i.r. flux at the top of the atmosphere (50 km), at the tropopause (which is at ~ 13 km for a mid-latitude summer atmosphere) and at the surface. Our model is compatible with the ICRCCM (Intercomparison of Radiation Codes in Climate Models²⁶) and the mid-latitude summer atmosphere of McClatchey et al.,²⁷ and is restricted to the clear-sky case.

The change in the net i.r. flux at the wavenumber ν and altitude z may be written as

$$\Delta F_{\nu}(z) = \pi B_{\nu}(T_s) A[z/\mu] + \pi \int_0^z B_{\nu}(T) dA[(z - z')/\mu] + \pi \int_z^{z_0} B_{\nu}(T) dA[(z' - z)/\mu]. \quad (5)$$

Here, $A(z)$ is the band absorptance, T_s the surface temperature, z_0 refers to the top of the atmosphere, B_{ν} is Planck's function, and μ the cosine of the zenith angle. Hemispherical averaging is performed using an eight-point Gaussian quadrature. $\Delta F_{\nu}(z)$ is defined so that it is positive for a reduction in the net upward flux.

Based upon measured vertical profiles,^{23,24} the atmospheric mixing ratios of CFC-11 and CFC-12 have been assumed to be constant up to 15 km and equal to 1 ppbv. Above 15 km, we have assigned scale heights of 3 and 5 km to CFC-11 and CFC-12, respectively. Our results for the reduction in the net upward flux due to the absorption in the 9.2 and 11.8 μm bands of CFC-11 and the 8.6, 9.1, and 10.8 μm bands of CFC-12 are presented in Table 1 for mixing ratios of 1 ppbv. Table 1 also contains a comparison between two calculations, in one of which the k_{ν} are assumed to be T -dependent according to Eq. (3). The effect of introducing the temperature dependence of the absorption coefficients is rather small as far as the flux reduction at the tropopause is concerned. It is about 8% in the case of CFC-11 and 2–3% in the case of CFC-12.

These results cannot be predicted without calculations based upon actual laboratory data. One of the aims of this investigation is to determine the effect of the temperature dependence of the hot bands on the atmospheric-fluxes. It is apparent from the present results that the effect is small. Since a large number of T -dependent factors appear in Eq. (5), a simple explanation of our results cannot be given. A heuristic approach is to look for T -dependent factors that produce compensating effects. For instance, since band absorptance $A(u)$, the only spectroscopic parameter appearing explicitly in Eq. (5), depends upon the products $S_{\nu}u$ (optically-thin case) or $k_{\nu}u$ along with the band width⁶ $\Delta\nu_{\nu}(T)$ (non-linear case), it may be that the variation with T of u in the atmosphere offsets the variation of S_{ν} or k_{ν} with height $z(T)$. Since we have assumed that the mixing ratios are constant below 15 km, where the effect of T is significant in Table 2, u should, therefore, exhibit the same exponential decrease with z as the atmospheric pressure. Thus, as k_{ν} (or S_{ν}) increases with z in the dominant central region of each CFC band, the variation of the product $k_{\nu}u$ (or $S_{\nu}u$) with height

Table 1. Comparison of two sets of calculations involving T -dependent [$k_v(T)$] and T -independent [$k_v(300)$] absorption coefficients on the reduction in the clear-sky i.r. flux for the midlatitude summer atmosphere due to the 9.2 and 11.8 μm absorption bands of CFC-11 and the 8.6, 9.1, and 10.8 μm absorption bands of CFC-12. The CFC 11 mixing ratio is assumed to be 1.0×10^{-9} for $z < 15$ km and $1.0 \times 10^{-9} \exp[(15 - z)/3]$ for $z \geq 15$ km. The CFC-12 mixing ratio is assumed to be 1.0×10^{-9} for $z < 15$ km and $1.0 \times 10^{-9} \exp[(15 - z)/5]$ for $z \geq 15$ km.

CFC	Band	Case	Flux Reduction (W/m^2)		
			Top	Tropopause	Surface
CFC-11	9.2 μm	$k_v(300)$	0.109	0.092	0.143
		$k_v(T)$	0.100	0.085	0.136
	11.8 μm	$k_v(300)$	0.347	0.300	0.568
		$k_v(T)$	0.318	0.277	0.542
CFC-12	8.6-9.1 μm	$k_v(300)$	0.287	0.237	0.353
		$k_v(T)$	0.278	0.230	0.348
	10.8 μm	$k_v(300)$	0.294	0.246	0.441
		$k_v(T)$	0.287	0.241	0.435

may not be significant. The variation of Planck's function B_ν with T should also be considered, even if it is small at the ν and T discussed here.

The magnitude of the correction due to the T -dependence of the k_ν cannot be estimated by means of simplified temperature-correction procedures²⁸ and without access to laboratory data at low T . For instance, the assumption that $S_\nu \sim \sqrt{T}$ led Owens et al²⁸ to calculate a 14% reduction in the surface-troposphere heating. It is significantly larger than the reduction derived in the present investigation by using actual laboratory data at low temperatures. It is, therefore, apparent that the use of a simplified temperature-scaling procedure leads to appreciable errors.

No assessment of the potential radiative forcing of CFC-11 and CFC-12 can be complete without including the effect of the overlapping absorption by water vapor. Assuming the water vapor profile

Table 2. Comparison of calculations, involving the experimental T -dependent k_ν , on the reduction in the clear-sky i.r. flux for the midlatitude summer atmosphere due to the 9.2 and 11.8 μm absorption bands of CFC-11 and the 8.6, 9.1, and 10.8 μm absorption bands of CFC-12. In case 1, overlapping water vapor absorption is ignored. In case 2, only the overlapping lines of water vapor are included. In case 3, overlapping absorption due to lines as well as the continuum of water vapor are included. The CFC-11 mixing ratio is assumed to be 1.0×10^{-9} for $z < 15$ km and $1.0 \times 10^{-9} \exp[(15 - z)/3]$ for $z \geq 15$ km. The CFC-12 mixing ratio is assumed to be 1.0×10^{-9} for $z < 15$ km and $1.0 \times 10^{-9} \exp[(15 - z)/5]$ for $z \geq 15$ km.

CFC	Band	Case	Flux Reduction (W/m^2)		
			Top	Tropopause	Surface
CFC-11	9.2 μm	1	0.100	0.085	0.136
		2	0.096	0.081	0.118
		3	0.086	0.072	0.070
	11.8 μm	1	0.318	0.277	0.542
		2	0.293	0.254	0.423
		3	0.249	0.216	0.168
CFC-12	8.6-9.1 μm	1	0.278	0.230	0.348
		2	0.254	0.209	0.270
		3	0.230	0.189	0.167
	10.8 μm	1	0.287	0.241	0.435
		2	0.275	0.230	0.379
		3	0.238	0.198	0.178

of the mid-latitude atmosphere of McClatchey et al²⁷ below 15 km and a constant mixing ratio of 6.43 ppmv (4.0 ppm) above 15 km,²⁶ we have computed the flux reduction as follows.

The effect of water vapor lines is included by adapting a line-by-line procedure based upon the HITRAN compilation,¹⁷ the Voigt lineshape,¹⁹ a wavenumber integration interval of 0.01 cm⁻¹, and a 10 cm⁻¹ cut-off. The cut-off limits the neighboring lines of water vapor to only those that are situated within ± 10 cm⁻¹ of each wavenumber. The temperature dependence of the line intensities, $S(T)$ (cm-molecule⁻¹) is given by

$$S(T) = S_0 \left(\frac{T_0}{T} \right)^{1.5} \exp \left[\frac{hc}{k} E'' \left(\frac{1}{T_0} - \frac{1}{T} \right) \right], \quad (6)$$

where h is Planck's constant, c the speed of light in vacuum, k Boltzmann's constant, E'' the energy of the lower state, and S_0 the line intensity at $T_0 = 296$ K. Due to the lack of reliable experimental data on the temperature dependence of the air-broadened halfwidths of water vapor,²⁹ we had to assume that $\gamma \sim \sqrt{1/T}$, an assumption of little consequence in the present computations.

Absorption by water vapor in the 8–12 μ m region is not only due to individual lines but also a continuum. The nature of the water vapor continuum is a controversial topic.²⁹ In view of the prevailing controversy, an acceptable means of illustrating the effect of the continuum absorption upon our calculations may be the application of the empirical formula due to Roberts et al,³⁰ which is popular among climate modelers.³¹

Comparisons of the flux reductions due to the 9.2 and 11.8 μ m bands of CFC-11 and the 8.6, 9.1, and 10.8 μ m bands of CFC-12 are presented in Table 2 for three cases. In case 1, absorption by water vapor is not considered at all. In case 2, lines of water vapor alone are included. In case 3, we include absorption due to lines as well as the continuum of water vapor. If the overlapping absorption by water vapor is neglected, the flux reduction at the tropopause due to 1 ppbv of CFC-11 and CFC-12 each is 0.833 W/m². It becomes 0.875 W/m² if the T -dependence of k_v is also ignored. If the overlapping absorption due to the lines of water vapor alone is included, the flux reduction at the tropopause due to CFC-11 and CFC-12 is diminished by 0.059 W/m², which may be compared with 0.042 W/m² enhancement derived by neglecting both the T -dependence of the k_v of the CFCs and water vapor absorption and to 0.036 W/m² obtained for the case of optically-thin CFC absorption and negligible water vapor absorption. The introduction of the overlapping absorption by both the lines and the continuum of water vapor into the flux calculations diminishes the combined CFC-11 and CFC-12 flux reduction at the tropopause by 0.158 W/m².

The influence of the absorption due to water vapor on the radiative forcing due to CFC-11 and CFC-12 extends beyond the modification of the radiative heating of the surface-troposphere system. As shown in Table 2 water vapor continuum absorbs a substantial portion of the enhanced emission toward the surface due to the presence of CFC-11 and CFC-12. Similar results were obtained by Kiehl and Ramanathan³¹ for the case of overlapping CO₂ absorption with the water vapor continuum. Since the continuum absorption is proportional to the square of the partial pressure of water vapor,²⁹ it is most significant within the first few kilometers above the surface. Thus, the diminished CFC-11 and CFC-12 emission toward the surface is compensated by an accompanying enhancement in the lower tropospheric heating. The combined heating rates for 1 ppbv of CFC-11 and CFC-12 each in a mid-latitude summer atmosphere are compared in Fig. 3 for the case in which overlapping water vapor absorption is included with the case in which it is neglected altogether. It is evident from Fig. 3 that water vapor absorption influences the CFC-11 and CFC-12 tropospheric heating rates significantly.

We present in Table 3 similar results obtained for various model atmospheres of McClatchey et al²⁷ as well as for the U.S. Standard atmosphere.³² The net flux reductions at the top of the atmosphere, the tropopause, and the surface are presented in Table 3 as before for both the cases containing and neglecting the overlapping water vapor absorption. As far as the flux reduction at the tropopause is concerned, the effect of the overlapping water vapor absorption varies from about 2% for a subarctic winter atmosphere to about 35% for a tropical atmosphere. Since water vapor concentration varies significantly among the various model atmospheres, these results are as one would expect. Table 3 also shows the strong effect water vapor absorption has on CFC-emission toward the surface. It has been reported previously⁸ that the impact of the overlap between the

Table 3. Comparison of calculations, involving the experimental T -dependent k_v , on the reduction in the clear-sky i.r. flux for several model atmospheres due to the 9.2 and 11.8 μm absorption bands of CFC-11 and the 8.6, 9.1, and 10.8 μm absorption bands of CFC-12. Yes and No comments appearing in the second column indicate whether water vapor absorption has been considered or not. The CFC-11 mixing ratio is assumed to be 1.0×10^{-9} for $z < 15$ km and $1.0 \times 10^{-9} \exp[(15 - z)/3]$ for $z \geq 15$ km. The CFC-12 mixing ratio is assumed to be 1.0×10^{-9} for $z < 15$ km and $1.0 \times 10^{-9} \exp[(15 - z)/5]$ for $z \geq 15$ km.

Profile	H ₂ O Overlap	Flux Reduction (W/m ²)		
		Top	Tropopause	Surface
Tropical	No	1.159	1.112	1.543
	Yes	0.851	0.823	0.396
Mid-latitude Summer	No	0.983	0.833	1.461
	Yes	0.803	0.675	0.583
Subarctic Summer	No	0.875	0.685	1.279
	Yes	0.728	0.572	0.691
Mid-latitude Winter	No	0.616	0.487	1.050
	Yes	0.575	0.454	0.817
Subarctic Winter	No	0.363	0.298	0.863
	Yes	0.356	0.293	0.756
U.S. Standard	No	0.984	0.789	1.223
	Yes	0.858	0.685	0.825

CFC-11 and CFC-12 bands and the absorption bands of other trace gases is $\sim 15\%$. We can see this from Table 3 to be an oversimplification that could lead to appreciable errors.

We may compare the results of our calculations to those appearing in Table 6 of Ramanathan et al.⁶ in terms of the surface temperature change ΔT_s produced by the flux change ΔF at the tropopause through the relationship^{33,34}

$$\Delta T_s \simeq \lambda \Delta F. \quad (7)$$

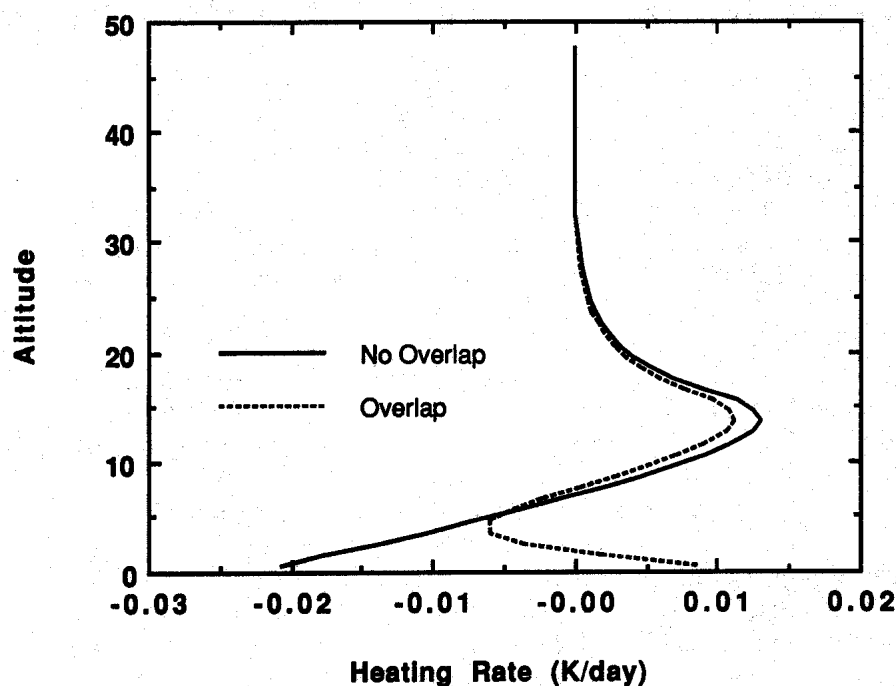


Fig. 3. The cumulative atmospheric heating rates due to 1 ppbv each of CFC-11 and CFC-12 in the midlatitude summer atmosphere of McClatchey et al.²⁷ (---) The case in which the effect due to the overlapping water vapor absorption is considered; (—) the case in which it is neglected.

λ is a climate sensitivity parameter which, according to the authors of Ref. 6, is equal to $0.52 \text{ K-m}^2 \text{ W}^{-1}$ for average global conditions.³² Kiehl has indicated³⁵ that the presence of clouds may be taken into account by decreasing the surface-troposphere forcing by 20% as in Ref. 6. By including the effect of clouds thus, we estimate ΔT_s amounting to 0.14 and 0.18 K, respectively, due to 1 ppbv of CFC-11 and CFC-12 each for the case where the overlapping water vapor absorption is neglected. We may compare these values to 0.16 and 0.19 K reported by Ramanathan et al.⁶ The difference between our results for the two cases and those of Ramanathan et al.⁶ is clearly due to the realism introduced in the present paper in the form of the T -dependence of the absorption coefficients of CFC-11 and CFC-12. For the case in which the overlapping water vapor absorption is considered, ΔT_s is 0.12 and 0.16 K, respectively, for 1 ppbv of CFC-11 and CFC-12 each. Ramanathan et al.⁶ reported 0.13 and 0.15 K for the corresponding cases. The agreement between our results and those derived by Ramanathan et al.⁶ are within the accuracy of the empirical treatment of the absorption by water vapor in the atmospheric window and of clouds.

Even though a number of other trace gases, CO_2 , O_3 , and N_2O being the most prominent, have absorption bands in the spectral region considered here, additional calculations³⁶ based upon available experimental data indicate that only the overlap between the absorption due to water vapor and the bands of CFC-11 and CFC-12 is significant.

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